SUMMARY

The carbohydrate complex of the Chara alga Chara aculeolata Kütz includes an acid polysaccharide similar to the pectin substances of higher plants. It is based on a fragment constructed of \(\alpha-1\rightarrow4\) bound residues of D-galacturonic acid in the pyranose form. The pectin is characterized by a high homogeneity, a considerable content of D-galacturonic acid, and a low degree of acidification of the carboxy groups.

LITERATURE CITED


EPOXY ACIDS OF THE SEED OIL OF Artemisia absinthium

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The seed oil of Artemisia absinthium (common wormwood) has previously been found to contain about 15% of epoxy acids, on the total acids present in the form of acyl radicals in the triglycerides [1, 2]. The unusually high content of epoxy acids attracted our attention to this source of vernolic and coronaric acids. However, in the seed oil of plants of this species growing in Central Asia we detected no signals of the protons of an epoxide ring by nuclear magnetic resonance (NMR) while at the same time the IR spectrum of the oil showed a region of absorption of the vibrations of the bonds of an epoxide ring. The reason for this may be a content of epoxy acids considerably smaller than 15%.

To determine the concentration more accurately and for use as standards in the investigation of other plants we studied the structure of the epoxy acids of the seed oils of the Central Asian wormwood. The oil was subjected to transesterification with methanol in the presence of sodium methoxide and the mixture of methyl esters (MEs) of the fatty acids was isolated. By thin-layer chromatography (TLC) on Silufol plates (system 1) followed by treatment with picric acid, the mixture obtained was found to contain two sharp zones of the MEs of epoxy acids. Then the mixture of MEs (50 g) was transferred to a column 3 cm in diameter filled with silica gel (100 mesh) to a height of 10-15 cm. The MEs of the unsubstituted fatty acids were eluted with light petroleum ether (the process was monitored on Silufol plates in system 1).

The methyl esters of the oxy acids (acids in which an atom or atoms of hydrogen are the aliphatic chain are replaced by oxygen or a hydroxy group) were eluted from the column with diethyl ether. The resulting concentrate of oxy acids, containing MEs of unsubstituted fatty acids as impurities, was separated in an ascending chromatographic column (system 1). This gave two fractions of MEs of epoxy acids (Fig. 1a), each of which was subjected to TLC on silica gel (100 mesh) impregnated with 20% of silver nitrate in system 2. When the chromatograms were treated with iodine, sulfuric acid, and the picric acid reagent, a slowly moving zone was found to contain a mixture of MEs of unsaturated epoxy acids (II) and traces
Fig. 1. Thin-layer chromatography of the methyl esters of the epoxy acids.

of MEs of saturated epoxy acids (III) (Fig. 1b). The two components were isolated separately by preparative TLC with silver nitrate in the same system.

Methyl Ester of Epoxy Acid (I): mol. wt. 310 (mass spectrum). IR spectrum, \( \nu_{\text{max}} \), cm\(^{-1}\): 2940 s, 1410 m, 1385 m (CH\(_3\)\(-\)); 2867 s, 1460 s, 730 m (\(-\text{CH}_2\)-); 1750 s, 1440 m, 1370 m, 1255 s, 1210 s, 1180 s, 1120 m, 1025 m (\(-\text{CH}_2\text{COOCH}_3\)); 3025 w, 1663 w, 767 s (cis –\(\text{CH}=\text{CH}\)–); 843 s, 837 s (epoxy group). NMR spectrum, \( \delta \) scale, in deuterochloroform: triplet of the protons of a methyl group at 0.9 ppm (3 H); multiplet of equivalent protons of isolated methylene groups at 1.31 ppm (16 H); signals of nonequivalent methylene protons (\(-\text{CH}_2\text{CH}=\), \(-\text{CH}_2\text{OOC}-\) and \(-\text{CH}_2\text{CH}-\text{CH}(-)\) in the 1.5-2.3 ppm region; multiplet of the protons of a cis epoxy group at 2.87 ppm (2 H); singlet of the protons of a methoxy group at 3.54 ppm; broad multiplet of the protons of an isolated ethylenic bond at 5.4 ppm, J = 28 Hz.

The oxidative degradation of the (I) was performed by the periodate-permanganate reagent followed by the methylation of the degradation products with diazomethane.

Gas–liquid chromatography (GLC) at 204°C, monitored in thin layers of cellulose (system 3), showed that the only degradation fragment not containing an epoxide ring was dimethyl azelate. This shows the position of the ethylene bond on the side of the ester end, as in methyl vernolate:

\[
\text{CH}_3(\text{CH}_2)_{\text{CH}}-\text{CH}\text{CH}_2\text{CH}-\text{CH}_2\text{CH}._{\text{COOCH}_3}
\]

Methyl Ester of Epoxy Acid (II): molecular weight 310 (mass spectrum). The IR and NMR spectra were identical with those given above. The only degradation fragment not containing an epoxy group detected by GLC at 123°C (monitoring in a thin layer of cellulose) was methyl caproate. Consequently, the ethylenic bond is on the side of the methyl end, as in methyl coronarotate:

\[
\text{CH}_3(\text{CH}_3)_2\text{CH}._{\text{CH}\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_3\text{COOCH}_3}
\]

The observed positions of the epoxide groups in the position isomers (I) and (II) correspond to their migration characteristics (see Fig. 1a), since of the two unsaturated epoxy esters the least mobile is that in which the epoxide ring is located on the side of the ester end [3].